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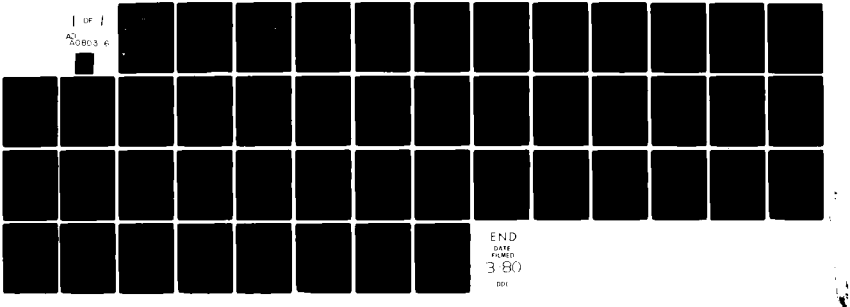

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LIQUID CHROMATOGRAPHIC ANALYSIS OF HYDRAULIC FLUIDS

GARY L. HAGNAUER and BEVERLEY M. BOWSE
POLYMER RESEARCH DIVISION

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November 1979

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ABSTRACT

High performance liquid chromatography (HPLC) is a versatile analytical technique for the separation and detection of components in complex chemical mixtures. HPLC test methods are developed to fingerprint the chemical compositions and to quantitatively analyze specific components in hydraulic fluids. Petroleum-base and synthetic hydrocarbon-base hydraulic fluids conforming to existing Military Specifications and used by the U.S. Army Materiel Development and Readiness Command are considered in this report. Detailed methods and test procedures are developed for the analysis of a MIL-H-6083D hydraulic fluid. The precision and accuracy of each method is evaluated. Suggestions are made regarding the implementation of the methods in Military Specifications, in field testing, and in the development of hydraulic fluids.

CONTENTS

SYMBOLS AND ABBREVIATIONS

A - integrated peak area or absorbance
Å - Angstrom, 10^{-10} meter
a_λ - molar absorptivity at wavelength λ
ATTN - attenuation
ASTM - American Society for Testing and Materials
AUFS - absorbance units full-scale
b - detector cell pathlength
BPC - di-tert-butyl-p-cresol
C - concentration or Celsius
C8 - 2,2,4-trimethylpentane
C18 - octadecyl group
cc - cubic centimeter
cm - centimeter
cs - centistokes, 10^{-2} poise/density (g/cc), 10^{-2} sec^{-1}
d - density
F - Fahrenheit
ft - feet
g - gram
GPC - gel permeation chromatography
GRAD - gradient in solvent programming
H - peak height
HPLC - high performance liquid chromatography
in. - inch
M - meter
min - minute
ml - milliliter, 10^{-3} liter
mm - millimeter, 10^{-3} meter
mV - millivolt, 10^{-3} volt
N - plate count
nm - nanometer, 10^{-9} meter
RI - refractive index or differential refractive index detector
sec - second
t - time
TCP - tricresyl phosphate
THF - tetrahydrofuran
UV - ultraviolet or ultraviolet detector
V - injection volume
VI - viscosity index
W or w - mass
wt % - weight percent
μ or μM - micrometer, 10^{-6} meter
μg - microgram, 10^{-6} gram
μl - microliter, 10^{-6} liter

I. INTRODUCTION

Most hydraulic fluids are complex chemical mixtures of a petroleum- or nonpetroleum-base stock component formulated with various additives which may be present in trace amounts or constitute up to 20% by weight of the fluid. The performance, stability, compatibility, toxicity, and flammability of a hydraulic fluid are directly related to its chemical composition. Hydraulic fluid additives include viscosity-temperature coefficient improvers, oxidation inhibitors, anti-wear agents, as well as corrosion and rust inhibitors. It is also noted that the fluids are susceptible to contamination and may undergo chemical changes during use and storage as evidenced by loss of volatiles, sludge formation, color changes, and hydraulic system failures.

Formulation sheets and samples of the fluid base stock and additives are required for qualification in hydraulic fluid Military Specifications. While some specifications are definitive with respect to the chemistry or required amounts of certain components and may even state what chemicals shall not be present, the chemical compositions of the fluid base stock and additives generally are not well specified. Also, inspection procedures tend to address the performance of a fluid rather than its chemical composition. Test methods to evaluate the overall composition or to quantitatively analyze specific components are not included or referenced in hydraulic fluid Military Specifications.

The need for the development of test methods to monitor chemical composition is evident when hydraulic fluid problem areas are considered. Since specification values for composition are only limiting values, the compositions of hydraulic fluids obtained from different suppliers may differ considerably.[1] Furthermore, the chemical compositions of additives may vary and formulation changes may be made but not reported. Such changes could have catastrophic effects on hydraulic system performance.[2] It is sometimes difficult to identify the specific hydraulic fluid being used and system failures may result from the inadvertent use of the wrong specification product or by mixing products from different suppliers. Fluid compatibility with seals and other system components also may be a problem if fluid composition is not well defined or if it should change during use. Contamination during fluid changeover can be a source of problems; e.g., incomplete fluid replacement in tanks retrofitted with a fire-resistant, hydrocarbon-base hydraulic fluid could be a fire hazard.[3] In addition, the Army stores and uses hydraulic fluids under conditions of wide climatic and environmental variations and severe operating conditions may be encountered - all of which may compromise the chemical composition and therefore the operational lifetime of a fluid.

The intent of this report is to suggest the implementation of a relatively new analytical technique, high performance liquid chromatography, as an inspection method to monitor the chemical compositions of hydraulic fluids. Test procedures

1. *Engineering Design Handbook Hydraulic Fluids*, AMCP 706-123, Headquarters, U.S. Army Materiel Command, April 1971, p. 4-3.
2. MESSINA, J. *Status Report on Using MIL-H-46170, Hydraulic Fluid, Rust Inhibited, Synthetic Hydrocarbon Base in M60A1 Tanks*. NASA TMX-73, v. 142, S. R. Riccitiello, ed., August 1976, p. 171.
3. JAMISON, R. G. *Determination of Contaminants in Less Flamable Hydraulic Fluids*. MERADCOM-2192, AD-A034751, September 1976.

are developed to "fingerprint" the overall chemical composition and to quantitatively analyze specific fluid components. A variety of fluids are examined and a case study is performed on a MIL-H-6083D hydraulic fluid of known formulation. Test criteria are established and a statistical evaluation is made of each test method. Inspection procedures described in this report are directly applicable for implementation in Army problem areas which include:

1. Specifications and procurement.
2. Monitoring fluid changeover.
3. Monitoring specific fluid contaminants.
4. Testing to determine when fluids need replacement or replenishment.
5. Trouble-shooting hydraulic system failures.
6. Developing and evaluating new or modified fluids.

High performance liquid chromatography (HPLC) is a versatile, analytical technique for the separation and detection of components in complex chemical mixtures. Recent advances in liquid chromatography have resulted in improved and automated instrumentation that is relatively low cost and simple to operate. The technique is ideally suited for the rapid and quantitative analysis of hydraulic fluids. Samples may be injected directly into the liquid chromatograph without elaborate sample preparation, and analyses may be obtained in minutes using quite small amounts (microliter) of sample.

Petroleum-base and synthetic hydrocarbon-base hydraulic fluids conforming to existing Military Specifications and used by the Development and Readiness Command (DARCOM) are considered in this report. The main body of the report concerns the development and application of HPLC test methods to fingerprint the chemical compositions and to quantitatively analyze specific components of hydraulic fluids. Suggestions are made regarding the possible implementation of such methods. Experimental details and test procedures are given in the Appendixes.

II. EXPERIMENTAL

A. Materials

The Military Specification designations and requirements concerned with chemical composition for the hydraulic fluids examined in this study are listed in Table 1.* The fluids were obtained from a number of different manufacturers through the U.S. Army Mobility Equipment R&D Center, Fort Belvoir, Virginia, and Frankford Arsenal, Philadelphia, Pennsylvania. Fluid samples are identified by their specification number rather than the manufacturer's designation. Fluids

*The latest revisions and amendments of the above specifications are:

MIL-H-5606D (1)	– Specification Date:	26 January 1978, Amendment Date: 10 March 1978
MIL-H-6083D (1)	– Specification Date:	28 September 1973, Amendment Date: 23 July 1976
MIL-H-83282A (1)	– Specification Date:	22 February 1974, Amendment Date: 10 September 1976 (for Air Force use only)
MIL-H-46170 (1)	Specification Date:	28 March 1975, Amendment Date: 8 June 1976

with the same specification number but obtained from different manufacturers are denoted, for example, as 46170-1 and 46170-2. A MIL-H-6083D fluid was obtained with samples of the base oil stock and additives and a formulation sheet describing the percentage and nature of each ingredient. The supplier's fluid (6083D-0) and fluids formulated (6083D-1 and -2) and off-formulated (6083D-3 to -7) in the laboratory using the manufacturer's components are shown in Table 2. The base oil is designated as a mineral oil. Tricresyl phosphate (TCP) is the antiwear agent and di-tert-butyl-p-cresol (BPC) is the oxidation inhibitor. The rust inhibitor consists of a 50 wt % solution of barium dinonylnaphthalene sulfonate in solvent-extracted castor oil. The sample number, density, and viscosity for each commercial fluid considered in this report are given in Table 3.

Table 1. HYDRAULIC FLUID SPECIFICATIONS

MIL-H-5606C	Hydraulic Fluid, Petroleum Base, Aircraft, Missile, and Ordnance – 30 September 1971
	Petroleum base oil stock Viscosity improvers – polymeric materials not to exceed 20 wt% Oxidation inhibitors – not to exceed 2 wt% Antiwear agent – 0.5±0.1 wt% tricresyl phosphate Red dye – not to exceed 1 part per 10,000 parts of oil by weight Pour point depressant materials shall not be used
MIL-H-6083C	Hydraulic Fluid, Petroleum Base, for Preservation and Testing – 17 November 1965
	Petroleum base oil stock Viscosity improvers – acrylic polymeric materials not to exceed 20 wt% Corrosion inhibitors – whatever quantity is necessary to comply with the corrosion property requirements Antiwear agent – 0.5±0.1 wt% tricresyl phosphate Dye – not to exceed 1 part per 10,000 parts of fluid by weight Pour point depressants shall not be used
MIL-H-6083D	Hydraulic Fluid, Petroleum Base, for Preservation and Operation – 28 September 1973 (Superseding MIL-H-6083C 17 November 1965)
	Petroleum base oil stock Viscosity improvers – acrylic polymeric materials not to exceed 20 wt% Oxidation inhibitors – not to exceed 2 wt% Corrosion inhibitors – whatever quantity is necessary to comply with the corrosion property requirements Antiwear agent – 0.5±0.1 wt% tricresyl phosphate Dye – not to exceed 1 part per 10,000 parts of fluid by weight Pour point depressants shall not be used
MIL-H-83282A	Hydraulic Fluid, Fire Resistant Synthetic Hydrocarbon Base, Aircraft – 22 February 1974
	Synthetic hydrocarbon base oil stock Additives – no restriction on the types of materials used for those except specifically restricted and those imposed by technical requirements Oxidation inhibitors – not to exceed 2 wt% Antiwear agent – agents such as tricresyl phosphate blended in sufficient quantity to meet lubricity requirements No pour point depressant materials or viscosity index improvers shall be used Water – less than 100 ppm total water
MIL-H-46170	Hydraulic Fluid, Rust Inhibited, Fire-Resistant, Synthetic Hydrocarbon Base – 28 March 1975/8 June 1976
	Synthetic hydrocarbon base oil stock-alpha-olefin polymer Additives – no restriction on the types of materials used except for those specifically restricted and those imposed by technical requirements (1.75±0.25 wt% barium dinonylnaphthalene-sulfonate provides the required degree of rust protection) No pour point depressant or viscosity index improver shall be used No resins, gums, fatty oils, oxidized hydrocarbons, chlorine or silica shall be contained in the fluid

Table 2. 6083D FLUID FORMULATIONS (WT%)

Sample	Base Oil	V.I. Improver	TCP	BPC	Rust Inhibitor
6083D-0	79.7	13.3	0.5	0.9	5.6
6083D-1	79.6	13.39	0.503	0.90	5.59
6083D-2	79.6	13.40	0.502	0.90	5.59
6083D-3	83.1	11.10	0.416	0.748	4.66
6083D-4	73.7	19.78	0.463	0.833	5.18
6083D-5	79.3	13.23	0.964	0.896	5.57
6083D-6	79.0	13.18	0.496	1.78	5.55
6083D-7	75.2	12.55	0.472	0.849	10.95

Table 3. HYDRAULIC FLUIDS

Sample	Color	Density (g/cc)*	Viscosity (cs)+ Experimental	Specified
5606C	red	0.8664	23.7	14.0 min
6083C	red	.8668	37.0	14.0 min
6083D	red	.8598	14.1	14.0 min
83282A	light yellow	.8481	15.5	14.0 min
46170-1	yellow-gold	.8515	16.6	18.5 max
46170-2	yellow-gold	.8579	16.6	18.5 max

*Density at 22 C
+Viscosity in centistokes at 100 F (37.8 C)

B. Solvents

High-purity, particulate-free solvents are required for liquid chromatographic analysis. Distilled in glass, 2,2,4-trimethylpentane (C8) and methylene chloride were obtained from Burdick & Jackson Labs, Muskegon, Michigan. Tetrahydrofuran (THF) was dried with molecular sieves and distilled from calcium hydride prior to solution preparation and HPLC analysis. Water was freshly distilled prior to its use in the LC and was not retained more than one day. All solvents were filtered under vacuum through 0.45 μ Millipore filters to degas and remove particulate matter. The organic solvents were kept dry and all solvents were stirred continuously to insure homogeneity during analysis.

C. Instrumentation

A Waters ALC/GPC-244 instrument with 6000A solvent delivery system, U6K injector, 660 solvent programmer, 440 dual wavelength UV absorbance detector, and R400 refractive index (RI) detector was used for most of the liquid chromatographic analyses. This system was used with Waters μStyragel, μPorasil, and μBondapak C_{18} columns to perform LC separations.

Some tests were designed using a Laboratory Data Control (LDC) model 709 solvent pumping station with a constant volume sample injector and a model 1103 refractive index detector. This system employed 4' × 3/8" Styragel columns.

The liquid chromatographs were interfaced for direct data analysis with a Spectra-Physics SP4000 data system which includes an SP4020 data interface, an SP4050 printer/plotter, and an SP4010 disc memory module.

III. DISCUSSION

A. GPC Fingerprinting

Gel permeation chromatography (GPC), also known as liquid exclusion or size exclusion chromatography, is a form of liquid chromatography that involves the separation of molecular species according to their size in solution. The column packing in GPC is usually in the form of microporous beads of silica or cross-linked polystyrene. The separation of molecules is a physical sorting according to size and takes place predominantly in the pores of the column packing. After a sample is injected and as it travels through the column(s), very large molecules (i.e., larger than the diameter of the largest pore size) are prevented by their size from entering the pores and therefore are restricted to the interstitial space in the solvent outside the porous beads. Smaller molecules permeate into and out of pores to a greater or lesser extent depending upon their size and upon the distribution of pore sizes available to them. Consequently, very large molecules are not retained and are eluted by an amount of solvent equivalent to the interstitial or void volume which is the sum of the column(s) and connective tubing volume not actually occupied by the packing particles. Smaller molecules have more volume (i.e., the pore volume) available to them and therefore require additional solvent for elution. The volume of solvent required to elute a particular molecule is inversely proportional to its size in solution. Very small molecules which are similar in size to the solvent molecules are retained longest and require the largest volume of solvent for elution. If the solvent flow rate is constant, the separation of sample components may be described either by their elution volumes or elution times. The terms retention volume and time are used synonymously with elution volume and time.

In order for the GPC separation mechanism to operate properly, specific interactions, e.g., adsorption between column or column substrate material and the sample components, must be prevented. Precautions must also be taken in solvent selection to assure sample solubility and to prevent the association of sample molecules into soluble aggregates. Such problems usually may be avoided by the judicious selection of column substrate, temperature, and solvent or solvent mixture. It is also noted that care must be taken in solvent selection because the substrate materials may be incompatible and ruined by contact with certain solvent types. If questions concerning solvent compatibility arise, it is advisable to consult the column manufacturer directly rather than risk damaging a column.

A variety of detectors are available to monitor the column effluent for sample components. A single detector or a set of detectors attached in series is connected by tubing directly to the column outlet. Generally, such detectors are designed to provide a signal proportional to the amount of material eluted although the detectability and response factor of a given component will differ according to its chemical structure and the chromatographic resolution obtained. The detector signal is usually transmitted to a recorder for visual display and perhaps an integrator for data analysis.

The most versatile and prevalent detectors in use today are the differential refractometer (RI) and the ultraviolet (UV) detectors. The RI detector responds to differences in refractive index between the column effluent and the eluent solvent reference such that only sample components with refractive indices different

from that of the solvent may be detected. For a given component, the detector signal is proportional to the refractive index difference as well as the component's concentration. The UV detector responds according to the Beer-Lambert relation, $A = a_\lambda bC$, such that the absorbance A or detector signal is directly proportional to the molar absorptivity a_λ of the component at the monitoring wavelength λ, the detector cell path length b, and the concentration C of the component. The UV detectors only monitor components that absorb UV radiation and provide the best response when the monitoring wavelength is selected near the absorbance peak maxima for the components of interest. Solvents that absorb UV radiation near the monitoring wavelength may swamp the detector signal and therefore should be avoided in UV detection.

The recorder trace of detector signal versus time provides a GPC chromatogram or fingerprint of sample composition based on molecular size and detectability. The fingerprint of a sample will vary depending on the type, size, and porosity of the column substrate. Other factors influencing the fingerprint are column design, column length, connective tubing, detector, injector, eluent, temperature, flow rate, sample size, and injection volume. All these factors should be considered and specified when reporting GPC fingerprints.

Tetrahydrofuran (THF) is an excellent eluent for the GPC fingerprinting of hydraulic fluids. High purity THF is commercially available for liquid chromatographic analysis. THF is compatible with column substrate materials and does not interfere with UV detection. All hydraulic fluids examined in this work were quite soluble in THF and could be injected directly for GPC analysis.

The chromatograms in Figure 1 were obtained using μStyragel columns with THF as the eluent. Significant differences are evident in the GPC fingerprints of 6083D-0 depending on whether RI or UV detection is employed. The base oil and VI

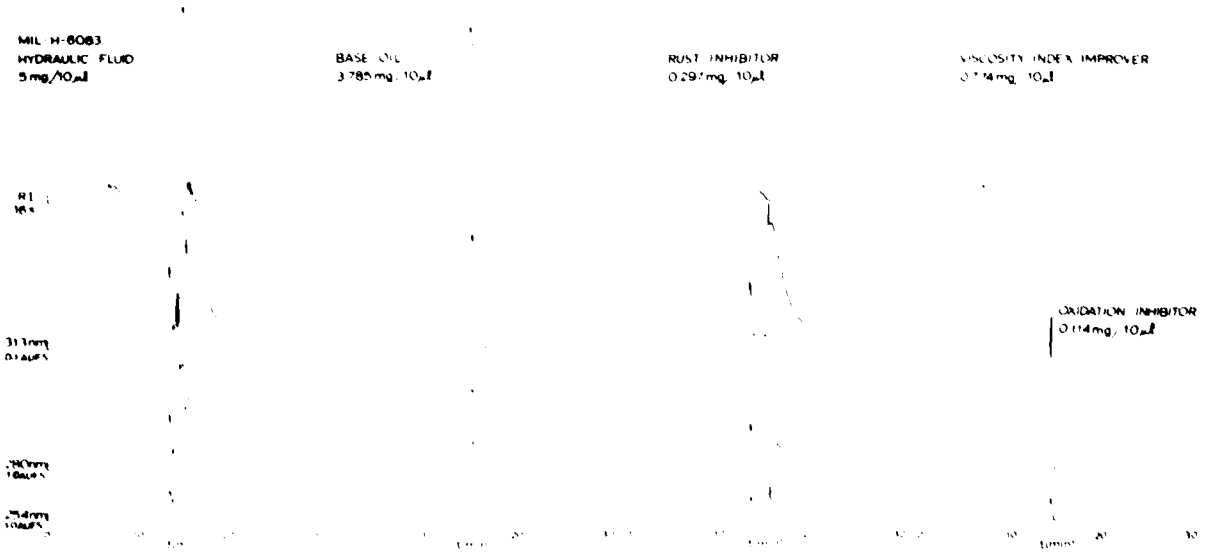

Figure 1. GPC fingerprinting.
μStyragel (10^3, 500, 500 Å); THF 2 ml/min; 10 μl injection

improver are best monitored using RI detection. The rust inhibitor has a rather complex composition and is most evident when monitored using 313-nm UV detection. The oxidation inhibitor is a minor component that has a retention time of 14.3 minutes and is best monitored using 280-nm UV detection. The polymeric component of the VI improver is partially excluded from entering pores in the column packing and therefore elutes early, starting at the exclusion limit (6.4 minutes). The VI improver elutes in the interstitial volume due to the selection of columns with low porosity (small pore size) packings.

GPC fingerprints of petroleum-base and synthetic hydrocarbon-base hydraulic fluids are compared in Figure 2. The fingerprints in Figure 2 were obtained using five μStyragel columns (10^3, 500, 500, 100, 100 Å); whereas three μStyragel columns (10^3, 500, 500 Å) were used to obtain the fingerprints in Figure 1. It is noted in comparing the 6083D fingerprints in Figures 1 and 2c that additional columns result in longer elution times and somewhat better resolution. The GPC fingerprints of the petroleum-base fluids are distinctly different from those based on synthetic hydrocarbons. Except for VI improver detection, the fingerprints obtained by UV monitoring offer more definition than those obtained using an RI monitor.

When an RI monitor is used, there is little ambiguity in establishing whether polymeric VI improver components are present in hydraulic fluids. For the five-column system, the VI improver starts eluting 11 minutes after injection, while other fluid components have elution times greater than 18 minutes. The UV monitor detects a rust inhibitor component at 19 minutes. The absence of this component is noted in the GPC fingerprints of 5606C and 83282A.

BPC has an elution time of 22 minutes and is a known component in 6083D. Oxidation inhibitors, such as BPC, are not prohibited from being incorporated in fluid formulations according to the Military Specifications under consideration; however, only MIL-H-5606C, -6083D, and -83282A specifically require oxidation inhibitors. Peaks appearing at 22 minutes occur in the UV monitored fingerprints of all the fluids. It is not necessarily the case that BPC or in fact any oxidation inhibitor be present in all the fingerprinted fluids. Unless the formulation chemistry is known and components used in the formulation are fingerprinted, it is not possible to state categorically that a peak appearing at a certain elution time is due to a particular component.

There may be a different component of similar size or more than one component being detected and contributing to a peak at the same elution time. If standards are available and the component of interest is resolved and readily detectable, such as BPC in 6083D, the relative concentration of the component can be discerned from its GPC fingerprint. For example, the relative amount of BPC apparently is smaller in 6083C than in 5606C or 6083D.

GPC fingerprints as characterized by peak elution times, heights, and shapes are highly reproducible. In replicate runs, peak elution times do not vary by more than 0.3% and peak heights agree within 2%. Fingerprints run a year later on the same samples are essentially superimposable. Although THF solutions were

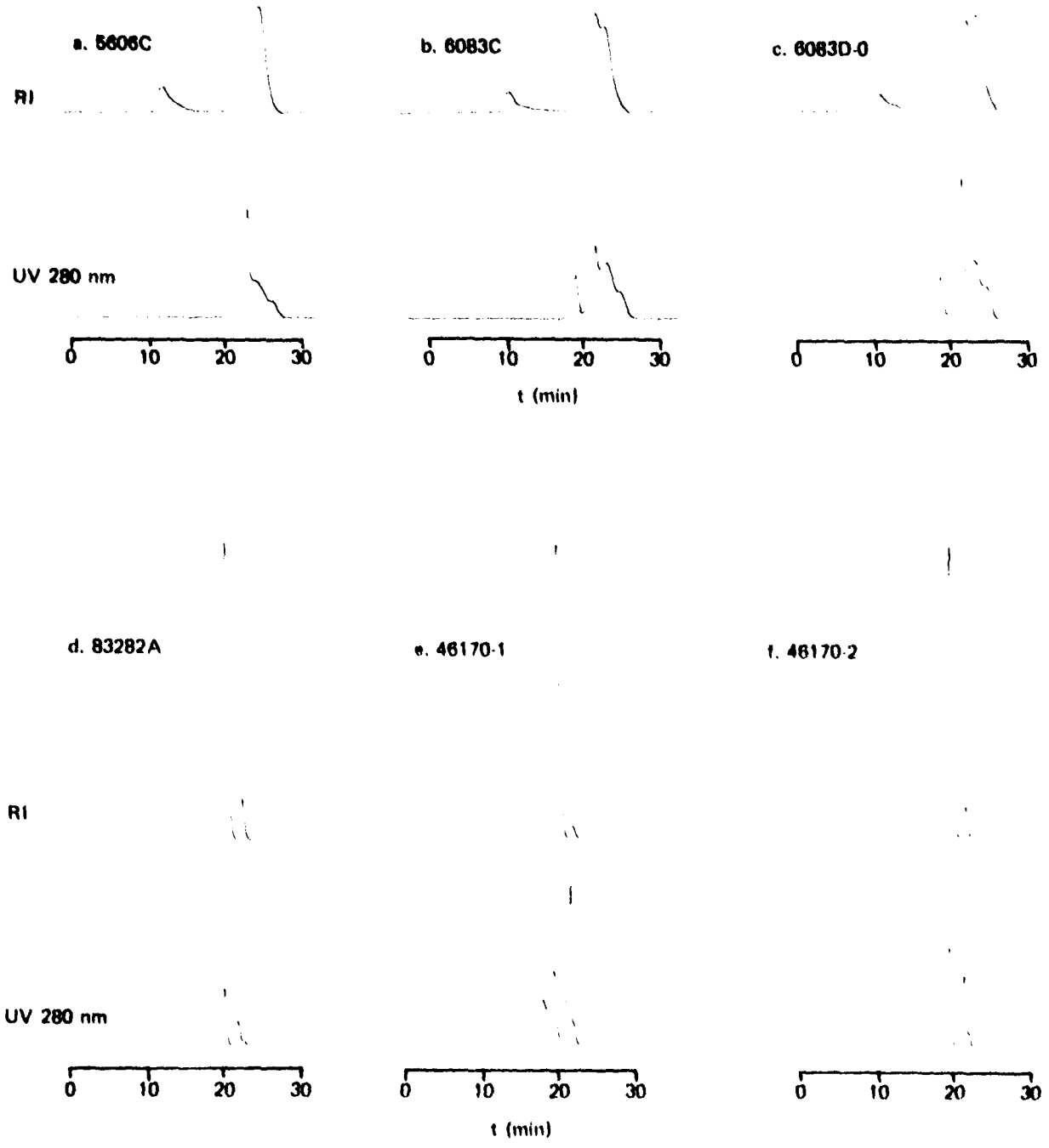

Figure 2. GPC fingerprinting.

μStyragel (10^3, 500, 500, 100, 100 Å); THF 2 ml/min;
100 μg/μl; 50 μl injection, RI 64X, ATTN 10;
10 μl injection, UV 280 nm, ATTN 10

analyzed in Figures 1 and 2, prior sample preparation generally is not required. Rather, since the fluids are completely soluble in THF, samples of 5 μ or less may be injected directly after filtration. Improved precision is possible when a closed-loop injector or an automatic injection system is used. Experimental details for GPC fingerprinting are given in Appendix A.

B. Viscosity Index (VI) Improver Analysis

The viscosity of a liquid decreases with increasing temperature and the extent to which viscosity changes with temperature depends on the chemical composition of the liquid. The viscosity index (VI) of a liquid is a number (ASTM Standards 1978, Designation D2270-77, Part 24, Philadelphia, American Society for Testing Materials, 1978) signifying the effect of a change in temperature on its viscosity. The larger the VI of a liquid, the less its viscosity will change with temperature. To perform over a wide temperature range hydraulic fluids generally must have a high VI. To meet this requirement high molecular weight polymeric additives, VI improvers, are often present in hydraulic fluids. Polymers and copolymers of methacrylates, olefins, butadiene, and styrene are used as VI improvers. The effectiveness of a VI improver depends on its chemical structure, concentration, molecular weight, and molecular weight distribution.

Military Specifications for hydraulic fluids do not specify the chemical structure, molecular weight, or molecular weight distribution of VI improvers. MIL-H-5606C, -6083C, and -6083D require only that polymer materials are not to exceed 20 wt %. MIL-H-6083C and MIL-H-6083D state that the VI improver must be an acrylic type polymer. MIL-H-83282A and -46170 specify that no VI improvers shall be present. Methods are needed to determine whether fluids contain VI improvers and, if so, what amounts. The methods should be rapid, require little sample, and be nondestructive. Two such methods are described below.

1. GPC Method

As discussed in Section III-A, VI improvers are polymeric and, by virtue of their size in solution, may be fully separated from other fluid components by GPC using columns with low porosity packing. Since the VI improver elutes in the interstitial volume, its retention time is highly reproducible. Using an RI detector to monitor column effluent, it is possible to quantitatively analyze the VI improver in hydraulic fluids. The concentration of the polymeric component is directly proportional to its peak height or integrated peak area. If a sample of the VI improver additive is available for calibrating detector response, the weight percent VI improver may be analyzed directly. Otherwise, if the additive is not available, the relative polymeric concentration may be evaluated by comparing the peak height or area of the unknown with the respective value of a standard or an acceptable formulation of the hydraulic fluid. In either case the hydraulic fluid may be injected directly or dissolved in a suitable solvent and then injected. Details concerning the method are given in Appendix B-1.

A relatively inexpensive apparatus consisting of a reciprocating pump with pulse damper, a closed-loop sample injector (0.2 ml), a 4-ft × 3/8-in. Styragel column (80-150Å), and an RI detector may be used for VI improver analysis. If a flowing reference is desired for the RI detector, a solvent splitter valve may be inserted between the pump and injector. No sample preparation is necessary. THF

is used as the mobile phase and the hydraulic fluid is filtered as it is loaded into the sample injector. The RI detector monitors the column effluent and its signal may be recorded and integrated. If a flow rate of 2.3 ml/min is maintained through the sample side of the detector, a chromatogram as shown in Figure 3 is obtained for 6083D-0. The retention time for the polymeric component is 609 seconds. Other components are noted at 764 and 1024 seconds. From a series of 10 runs, the average polymer peak retention time is 608 ± 1 seconds and its integrated peak area is 341 ± 11 mV-sec. The percent of the total integrated area represented by the polymer peak is 11.0 ± 0.1% and is more precise than the absolute peak area since it is less affected by slight differences in the injection volume.

If the solvent splitter valve is closed, the RI detector's solvent reference becomes static and the flow rate through the sample side increases to 3.3 ml/min. For 30 analyses of 6083D-0 run over a period of three days, the polymer peak retention time was exactly 429 seconds with an average area of 237 ± 9 mV-sec or 11.1 ± 0.3% based on the total integrated area. Although the increased flow rate decreases the analysis time to 14 minutes, it also results in poorer resolution and in slightly poorer precision.

To evaluate the accuracy of the GPC method which employs a static RI reference, samples of 6083D-0 were spiked with different amounts of VI improver and were analyzed using 6083D-0 (13.3 wt % VI improver) as the standard. Average values of weight percent VI improver based on peak area and peak area percent determinations are shown in Table 4. The standard deviation is given for each determination. The accuracy is quite good even at 20 wt % which is the maximum allowable VI improver concentration for petroleum-base fluids. Calculations based on absolute peak area are more reliable than those based on peak area percent in cases where nonpolymeric fluid components are subject to variation.

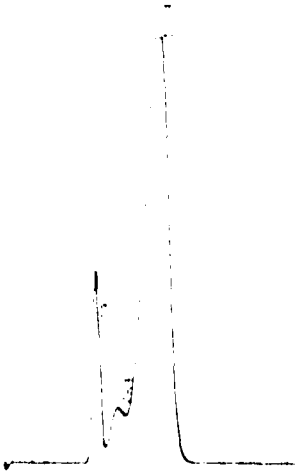

Figure 3. VI improver analysis - GPC method.

Styragel (80-150 Å) (4 ft x 3/8 in.); THF 2.3 ml/min; 0.2 ml 6083D-0

Table 4. VI IMPROVER (WT%) IN SPIKED 6083D-0

Actual	Calculated	
	peak area	peak area %
14.5	15.0 + 0.5	14.4 + 0.2
16.7	17.6 + 0.9	16.1 + 0.3
20.0	20.1 + 0.6	20.0 + 0.2

Although no difficulties were encountered in this study, resolution, solubility, solute-substrate interaction and detection, as discussed in Section III-A, are possible problem areas and should be considered before analyzing fluids of novel or unknown composition. Often such problems can be remedied by subtle changes in system parameters, such as columns, solvent, temperature, or detector. Finally, if a standard is not available, it may still be possible to perform quality control by comparing polymer peak areas relative to that of a fluid of acceptable composition.

2. Adsorption Chromatographic Method

Another approach to the quantitative analysis of VI improvers involves the use of a column with polar, microporous silica packing, THF as the mobile phase, and RI detection. After filtration, the hydraulic fluid is injected onto the column using a micro-syringe. Details are given in Appendix B-2. Analysis is completed in about two minutes (Figure 4) with the acryloid VI improver eluting one minute after injection as a sharp, well-resolved peak. The mechanism for this separation is subject to debate. It is noted that no other components are resolved from the second peak in the chromatograph(s). Due to its polarity, the use of THF as the mobile phase in adsorption chromatography generally results in low retention times and poor resolution. Actually, it is possible that neither a liquid-solid nor a liquid-liquid separation is involved, but rather that the separation of the VI improver is achieved by size exclusion due to the microporous nature of the column packing.

VI improver concentration is directly proportional to the height and area of its peak in the chromatogram. Either a standard hydraulic fluid or a set of standard acryloid polymer solutions with THF as the solvent may be used for calibration. Selecting 6083D-0 as the standard with 13.3 wt % VI improver, multiple analyses were run on different formulations. The precision is ±0.2 wt % for the peak area method and ±0.4 wt % for the peak height method. The agreement between formulated and measured weight percentages is +0.2 ± 0.4 wt % for the peak area method and -0.1 ± 0.7 wt % for the peak height method.

The major source of error in this method is caused by the operator's inability to precisely inject identical amounts of sample. This error could be reduced by employing a sample processor for automatic injection or by relying on an internal standard to correct for differences in injection volumes. An error is also introduced in measuring peak heights, ca. ± 0.5 mm or 0.3 wt %.

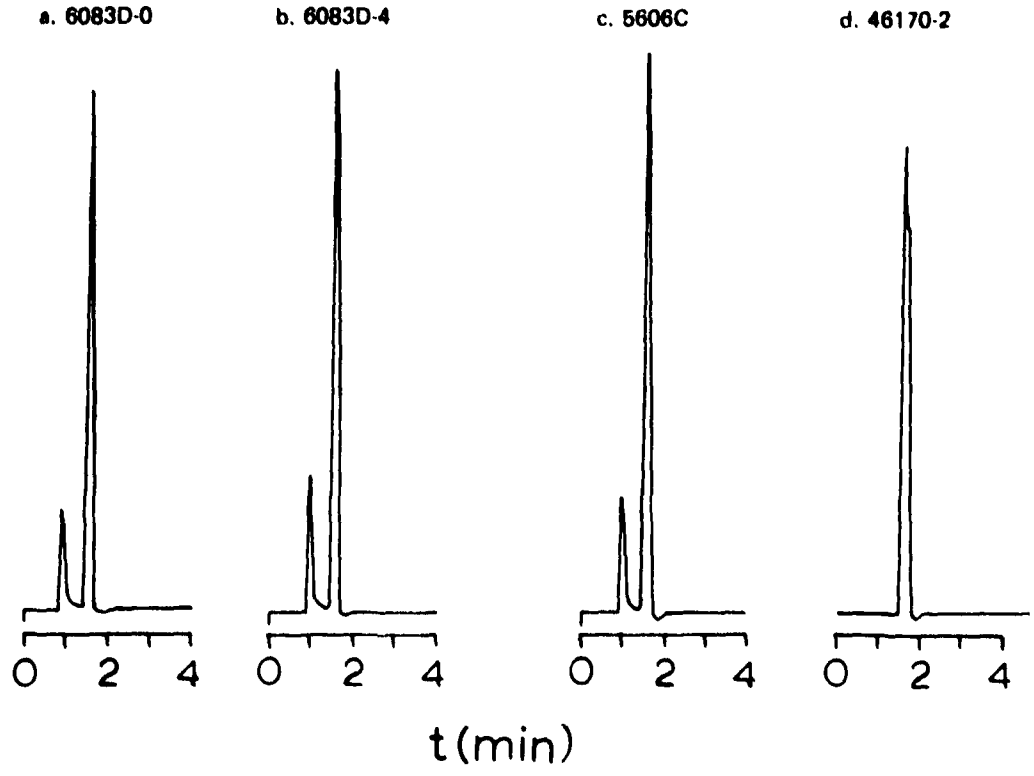

Figure 4. VI improver analysis - adsorption chromatography method.
μPorasil; THF 2 ml/min; 5 μl injection; RI 8X, ATTN 50

Results from the VI improver analysis of different fluids are shown in Table 5. The discrepancy between the formulated and measured values for samples 6083D-1, -2, -3, -4, and -7 may be due, in part, to weighing errors during formulation. At high VI improver concentrations peak spreading may become important, especially when determinations are based on the peak height method. The low VI improver value for 6083D-4 according to peak heights may be a consequence of this effect. Sample 6083D-0 (exposed) is an aliquot of sample 6083D-0 that was exposed to sunlight for a period of one month in an open container. The somewhat higher VI concentration of 6083D-0 (exposed) may be a consequence of the sample losing some of its more volatile components by evaporation or, perhaps, due to changes in the chemical structure of the VI improver which might also change its refractive index. The analyses of 6083C and 5606C are suspect since the identity of VI improver in each case is unknown. The disparity between peak area and height values suggests that 6083C and 5606C may indeed have VI improvers which are different in chemistry from that found in 6083D-0. Precautions must be taken when applying this method to be certain that the VI improver is actually separated and that no other components are contributing to the VI improver peak. Non-acryloid VI improvers will not necessarily be resolved. Chemical differences in fluid composition may obviate meaningful analysis.

Table 5. VI IMPROVER ANALYSIS-ADSORPTION LC

Sample	Formulated	WT% Measured by Peak Area	Peak Height
6083D-0	13.3	13.3 ± 0.2	13.3 ± 0.4
-1	13.4	14.0	13.6
-2	13.4	14.0	13.6
-3	11.1	11.1	11.8
-4	19.8	19.6	18.3
-7	12.6	12.4	12.3
6083D-0 (exposed)	13.3	13.8	15.0
6083C	unknown	12.3	10.6
5606C	unknown	17.7	15.5
83282A	unknown	0	0
46170-1	unknown	0	0
46170-2	unknown	0	0

C. Adsorption Chromatography Fingerprinting

Adsorption chromatography, also known as normal phase or liquid-solid chromatography, is a powerful technique for separation. Separation depends upon specific interactions between solute components and the stationary phase at the surface of the column packing. An adsorbent or polar packing (e.g., silica) is used and consists of pellicular or porous particles of small size. The packing has active sites with varying degrees of activity that provide retention of the solutes. Mobile phase molecules compete with the solute for adsorption sites. The mechanism for separation is subject to debate and no single "best" model describes all situations.

Mobile phase selection is critical. If the mobile phase is not sufficiently polar, extremely long retention times, peak tailing, and irreversible adsorption may occur. If the mobile phase is too polar, short retention times and poor resolution results. A good solvent of intermediate polarity and available in high purity is methylene chloride. The relative polarity or strength of the mobile phase may be adjusted by using mixtures of miscible solvents. Solvent programming techniques such as gradient elution also may be used to improve resolution and achieve complete elution. Gradient elution is a technique for increasing the solvent strength of the mobile phase as the separation proceeds. When an adsorbent packing is used, the composition of the solvent is programmed to increasing polarity.

Precautions must be taken when using adsorption chromatography. Immiscible solvents and solvents with highly polar constituents (e.g., water, alcohols, acids) must be avoided. The solvents should be pure and filtered, preferably under vacuum, to degas and remove particulates. Also, samples should be filtered and verified soluble in the mobile phase. Columns should be handled carefully and tested periodically with a standard test mixture under standard chromatographic conditions. If a standard batch of hydraulic fluid is used as the test mixture, small changes in peak position and resolution may be observed. Such changes are normal and reflect minor differences in solvent composition or pump performance. However, a large decrease in retention time or plate count may indicate that the adsorbent is

deactivated or that the column has been damaged. Often such columns can be regenerated and their plate counts restored by elution with sequence of solvents to remove built-up solvent impurities and strongly adsorbed sample components. If columns are damaged by plugging, voids in the packing, or irreversible adsorption, they sometimes can be salvaged by replacing the packing at the column inlet and cleaning the end frit. If, after several attempts to regenerate, a column still has a low plate count (<2000 plates) and contributes significantly to peak spreading, it should be discarded or repacked.

For adsorption chromatography, a widely accepted choice of packing material is porous silica gel having a surface area of 200-500 M^2/g and a particle size of 10 μM. High efficiency columns (>3000 plates) packed with porous silica are commercially available from a variety of manufacturers at competitive prices.

Since the components in hydraulic fluids cover a broad range of polarity, gradient elution is usually required for fingerprinting overall composition. Solvent programming by gradient elution will optimize separation and provide a definitive fingerprint within a short period of time. A variety of solvent compositions and gradients were considered in this work. Perhaps the simplest and most reliable technique involves the use of three μPorasil columns with the mobile phase run at a flow rate of 2 ml/min and programmed to change as a linear gradient from 100% iso-octane (C8) to 80%C8/20%THF over a period of 5 minutes (see Appendix C). No sample preparation is required. The fluid is loaded in the sample loop and the gradient is initiated upon injection. The fingerprint is obtained in 15 minutes as the signal recorded from a 280-nm UV detector.

Four such fingerprints are shown in Figure 5 with the retention time indicated after each peak in seconds. One way to determine the position of a particular component is to spike the hydraulic fluid sample with that component. For example, the fingerprint of 6083D-0 is shown in Figure 5c. The fingerprint in Figure 5a was obtained from the analysis of 6083D-7 which is 6083D-0 spiked with rust inhibitor. The peak having a retention time of 307 seconds is obviously a rust inhibitor component that absorbs at 280 nm. Similarly, the fingerprint of 6083D-6 in Figure 5b confirms that the peak appearing at about 500 seconds is due to the oxidation inhibitor BPC. The portion of the fingerprints between the rust inhibitor and BPC peaks is largely due to the base oil.

As a demonstration of how adsorption chromatography fingerprinting might be used to detect compositional changes, the fingerprint of 6083D-0 exposed to sunlight for one month is shown in Figure 5d. It is noted that the large peak due to BPC is no longer evident at 500 seconds and that a new peak appears at 714 seconds. The new peak is probably BPC transformed to a different chemical species due to the action of sunlight and oxidation. It is also noted that the new species is probably more polar than BPC since it has a longer retention time.

D. Adsorption Chromatography - Component Analysis

1. Gradient Elution - Base Oil, Rust, and Oxidation Inhibitors

Petroleum- and synthetic hydrocarbon-base oils are widely used in hydraulic fluid formulations. However, because of the variety of sources and possible variations in composition, the base oil is perhaps the most difficult component to

analyze adequately. HPLC fingerprinting shows that the chemical compositions of base oils generally are quite complex, containing an assortment of linear, branched, cyclic, and isomeric saturated and unsaturated hydrocarbons. Complete separation and analysis of such complex mixtures are impractical and not essential for purposes of identification and quality control. Indeed, because base oils have such complex compositions, their HPLC fingerprints tend to be unique. Therefore, it is relatively easy to distinguish between different types or sources of base oils.

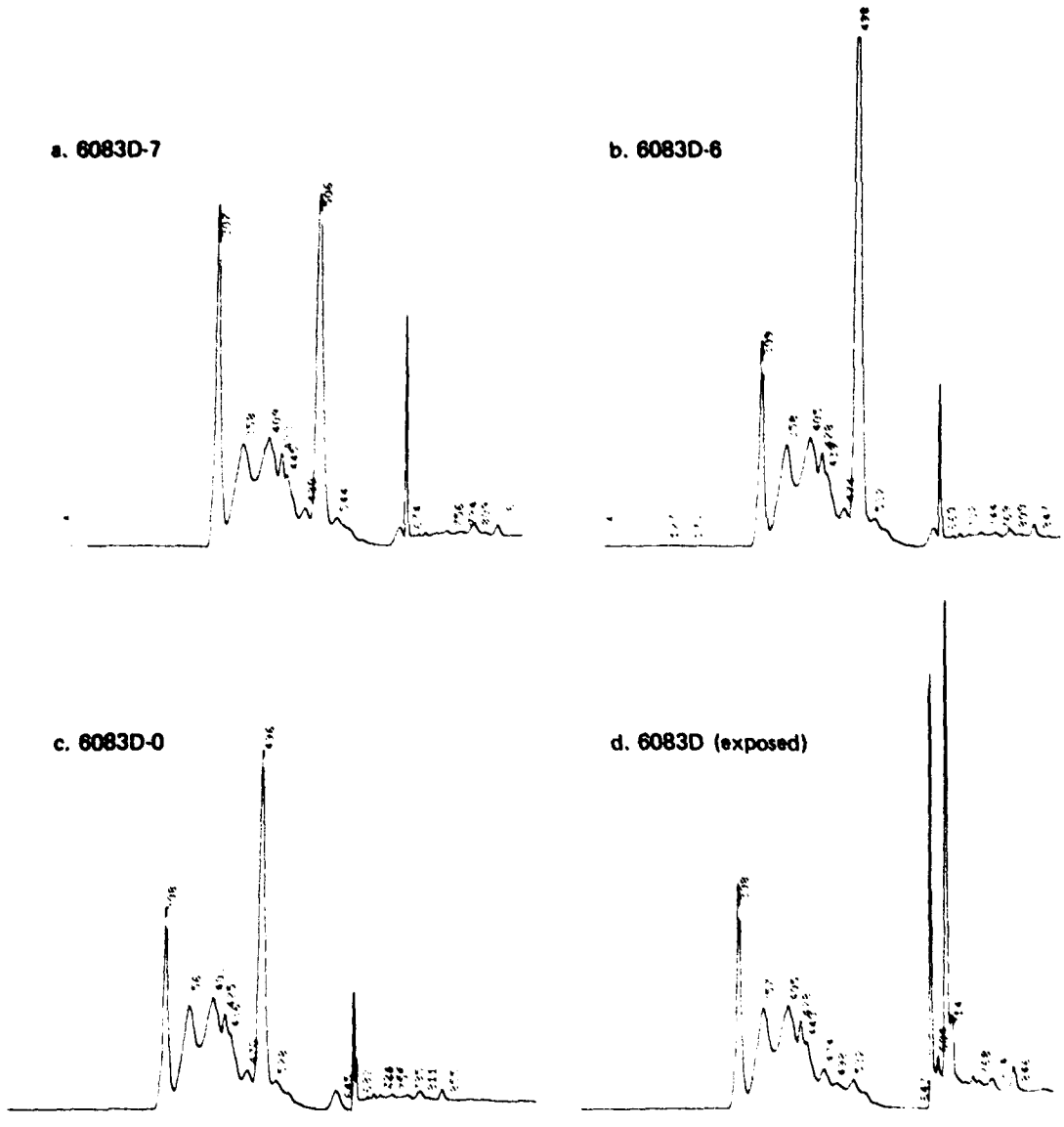

Figure 5. Adsorption chromatography with gradient elution.
μPorasil (4 mm x 90 cm); 100%C8 to 80%C8/20%THF; 5-min, GRAD 6;
2 ml/min; UV 280 nm; 1 AUFS; ATTN 10; 5 μl injection

However, it is difficult to obtain accurate quantitative analysis unless one has as a standard the actual base oil used in formulating the hydraulic fluid and unless the chromatogram of the standard has a well-resolved peak that can be monitored without interference by other components in the hydraulic fluid.

As an example, the base oil in 6083D-0 has a component eluting at 357 ± 2 seconds (Figure 5). By assuming that the base oil in 6083D-0 is proportional on a weight basis to the area or height of the 357 seconds peak and by spiking 6083D-0 with its base oil standard for calibration (see Appendix D), the weight percentages of base oil in 6083D-0 and off-formulations of 6083D-0 were calculated and are shown in Table 6. The repeatability of each determination is ±3.1%, whereas the agreement between the average values calculated and the formulated weight percent is somewhat better. The low value calculated for exposed 6083D-0 may be reflecting the loss of volatile base oil components or possibly chemical changes in the component eluting at 357 seconds.

Table 6. 6083D COMPONENT ANALYSIS*

ADSORPTION CHROMATOGRAPHY GRADIENT ELUTION

Sample	Base Oil	WT% Rust Inhibitor	BPC
6083D-0	78.5 (79.7)	5.2 (5.6)	0.90 (0.9)
6083D-1	79.6 (79.6)	6.1 (5.6)	.92 (0.90)
6083D-2	79.6 (79.6)	6.1 (5.6)	.88 (0.90)
6083D-3	84.5 (83.1)	3.7 (4.7)	.74 (0.75)
6083D-6	75.4 (79.0)	5.3 (5.6)	1.44 (1.78)
6083D-7	72.8 (75.2)	11.3 (11.0)	.97 (0.85)
6083D-0† (exposed)	65.5 (79.7)	8.9 (5.6)	.063 (0.9)

*Formulated compositions are given in parentheses.
†An aliquot of 6083D-0 that was exposed to sunlight in an open container for one month.

Rust and oxidation inhibitors are specific types of additives used to prevent corrosion which results from chemical attack on metal surfaces. Corrosive agents are ubiquitous (e.g., water) and may contaminate hydraulic fluids in a variety of ways; e.g., base oils may oxidize to form organic acids. Rust inhibitors are often organo-sulfonate or -amine derivatives. The polar functional groups of rust inhibitor molecules permit them to adsorb on metal surfaces and form hydrophobic films. The film acts as a protective barrier to prevent corrosion.

The 6083D-0 is formulated with barium dinonylnaphthalene sulfonate as the rust inhibitor. Using adsorption chromatography with gradient elution (Figure 5), the rust inhibitor is fully resolved and elutes as a sharp peak at 308 ± 1 second. If the peak spiking method is used for calibration, one obtains results as shown in Table 6 (see Appendix E). The precision of each determination is ±1.4%. The average difference between the formulated and calculated values is +0.07 wt % with a standard deviation of ±0.55 wt %. The high value determined for 6083D-0 (exposed) may be due to loss of the more volatile fluid components or to the formation of products which have retention times similar to that of the rust inhibitor.

Oxidation inhibitors increase the resistance of hydraulic fluids to chemical changes associated with oxidation. As a result of oxidation, organic acids, sludge, and varnish may form and viscosity changes may occur. Oxidation inhibitors suppress the effects of oxidation by reacting with free radicals to form stable products or by decomposing peroxides. Such inhibitors are usually aromatic amines, phenols, or sulfides. Also, organic phosphites, thiophosphates, and sulfides are used to inhibit oxidative catalysis by metal ions. The oxidation inhibitor in 6083D-0 is BPC (di-t-butyl-p-cresol). BPC has a large molar absorptivity at 280 nm and therefore can be detected and analyzed in 6083D-0 with a high degree of accuracy even though the fluid is formulated with less than 1 wt % BPC (see Appendix F). The BPC has a retention time of 500 ± 6 seconds and is not fully resolved from the base oil components. However, because its UV absorbance is much greater than that of the base oil components, the BPC level in 6083D-0 may be analyzed with high precision, ±2%. The agreement between the formulated and analytical BPC values in Table 6 is 0.04 ± 0.14 wt %. It is noted that the actual weight percent BPC for 6083D-0 (exposed) may be lower than indicated in Table 6. Base oil components contribute significantly to the 498 seconds peak area at low BPC concentrations.

2. Isocratic - Antiwear Additive Analysis

Hydraulic fluids form lubricating films to reduce friction and wear between contacting metal surfaces. Under adverse operating conditions of high pressure or temperature, the lubricating film can rupture and allow metal-to-metal contact. Antiwear additives prevent such contact by forming a protective coating on the metal surfaces. Heat generated by the friction between shearing surfaces provides energy for a chemical reaction between the additive and the metal to form the coating. Phosphates, phosphites, sulfides, and chlorinated organic compounds show antiwear properties in hydrocarbon-base fluids. Tricresyl phosphate (TCP) is specified as the antiwear agent in 5606C, 6083C, and 6083D-0 at 0.5 ± 0.1 wt %.

Adsorption chromatography provides a rapid, quantitative method for TCP analysis. The method (Appendix G) requires a μPorasil column, methylene chloride as the mobile phase, and a 254-nm UV detector. Samples may be injected directly or diluted with methylene chloride. The analysis time is 5 minutes with TCP eluting as a single, well-resolved peak at 275 ± 2 seconds. If undiluted samples are analyzed, calibration can be accomplished by the peak spiking method. Using this method and analyzing peak areas, the TCP concentration in 6083D-0 is 0.462 ± 0.014 wt %. The precision of this method is ±3.0% if values are determined by peak integration or ±4.4% if peak heights are measured.

The TCP method may be modified using benzyl alcohol as an internal standard to obtain higher precision. The internal standard reduces random errors associated with sample injection. Samples may be prepared for analysis by adding benzyl alcohol directly or as a solution with methylene chloride to the hydraulic fluid. Benzyl alcohol elutes as a fully resolved peak at 550 ± 5 seconds (Figure 6a). The data in Table 7 were obtained using the internal standard method and injecting samples diluted with methylene chloride. The standard deviation shown for 6083D-0 is typical for this method. The precision is ±1.01% using peak areas and ±1.2% from peak height measurements. The accuracy as determined from the difference between formulated and measured values of +0.009 ± 0.012 wt % by peak area and +0.009 ± 0.019 wt % by peak height measurements.

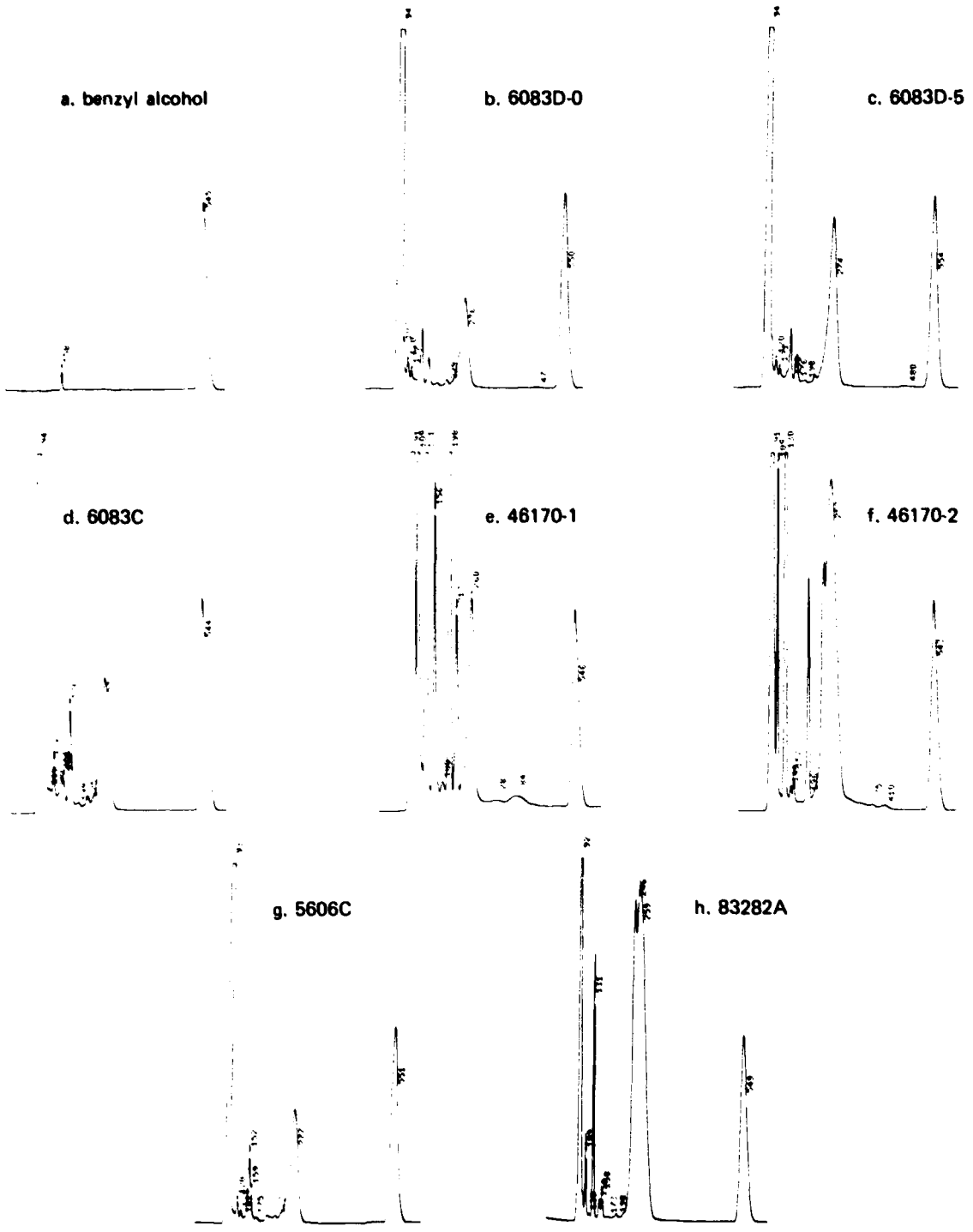

Figure 6. Adsorption chromatography - isocratic.

μPorasil (4 mm x 30 cm); methylene chloride; 2 ml/min; UV 254 nm; 0.2 AUFS; ATTN 10; 10 μl injection; internal standard: benzyl alcohol

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Table 7. TCP ANALYSIS-ADSORPTION CHROMATOGRAPHY

Sample	WT% Formulated	Measured peak areas	Measured peak heights
6083D-0	0.5	0.470 ± 0.004	0.49 ± 0.01
6083D-1	.503	.501	.48
6083D-2	.502	.504	.53
6083D-3	.416	.401	.40
6083D-5	.964	.963	.94
5606C	unknown	.615	.61
6083C	"	.661	.64
83282A	"	-	-
46170-1	"	-	-
46170-2	"	-	-

There are several different places where significant errors may be introduced in the TCP analysis. Statistical errors are associated with pipetting and measuring peak heights. If the fluid density or the volume change encountered during mixing is different from that for the hydraulic fluid standard, systematic errors may occur. Suggestions to circumvent these sources of error are given in Appendix G.

Chromatograms obtained from the TCP analysis of various hydraulic fluids are shown in Figure 6b-h. Definitive fingerprints are obtained for each sample. Apparently TCP is not an additive in 46170-1, 46170-2, or 83282A as indicated by the absence of the 275 seconds peak in their chromatograms. It is uncertain whether the peaks appearing at 257-260 seconds represent other types of organophosphate antiwear additives. Finally, it is noted that the TCP in 6083C is significantly higher than the specified value 0.5 ± 0.1 wt %.

E. Reverse Bonded-Phase Chromatography Fingerprinting

Bonded-phase chromatography is a type of liquid partition chromatography in which the stationary phase is chemically bonded to silica support material. The term reverse phase chromatography applies to the case where the bonded stationary phase is relatively nonpolar (e.g., an octadecyl or C18 group) and the mobile phase is more polar than the stationary phase. Separation is based on the relative solubility and distribution of the solute between the mobile and bonded phases such that solutes that are more soluble in the bonded phase tend to have longer retention times. In general, elution tends to be the reverse obtained by normal phase or adsorption chromatography. This means that components which elute early and are difficult to separate by normal phase chromatography tend to be retained and better separated in the reverse phase mode. Basically, the retention of a solute depends on its solubility and on the ratio of the volumes of the stationary and mobile phases. However, since other effects such as adsorption and association may also occur, an exact mechanism for bonded-phase chromatography is difficult to apply.

Bonded-phase columns are probably the least prone to problems in HPLC. The columns are compatible with a large variety of solvents and are capable of separating polar, nonpolar, and ionizable components in a single analysis. The columns achieve equilibrium rapidly and may be used with solvent programming. When used properly, the columns show very little irreversible retention and provide

long service. As with other HPLC modes, filtered, high quality solvents are required for analytical work. Care must be taken in handling to prevent void formation in the packing and the solvent pH must stay within the range of pH 2-8. Problems with repeatability or loss of column efficiency are generally due to the column becoming contaminated by sample precipitation or by the slow accumulation of highly nonpolar species in the bonded phase. Such contaminates may be removed by eluting the column with a strong solvent or by following the column manufacturers' suggested procedures.

A variety of high efficiency columns (>3000 plates) are commercially available for reverse bonded-phase chromatography. The packing material consists of porous microparticles (5 or 10 μM) of silica gel with a bonded-alkylated surface. Usually, the alkyl phase is bonded by reacting silanol groups on the surface of the silica gel with an alkyltrichlorosilane. The column used in this work (Waters Associates μBondapak C18) is packed with silica gel having a C18 silane bonded phase. The particle size is 10 μM with a narrow particle size distribution and a surface area of 300 to 500 M^2/g.

In reverse bonded-phase HPLC, the mobile phase generally consists of water mixed with a water miscible organic solvent. Frequently, water/methanol or water/acetonitrile mixtures are used. A variety of different solvents and solvent mixtures were examined for the separation and analysis of the hydraulic fluids in this study. Combinations of water/THF or water/methanol/THF gave the best results. Solvent programming techniques are used to improve the separation of components and to reduce contamination of the bonded phase. The solvent is programmed by gradient elution to increase the proportion of the organic solvent in the mobile phase.

Definitive fingerprints of hydraulic fluids are obtained using a single μBondapak C18 column with THF/H_2O as the mobile phase run at 2 ml/min and programmed to change as a linear gradient from 40% to 100% THF over a period of 15 minutes. No sample preparation is required. The fluid is injected directly onto the column and the gradient is initiated upon injection. A total run time of 30 minutes is required per analysis and re-equilibration. A 280-nm UV detector is used to monitor the column effluent.

As shown in Figure 7, significant differences are apparent in the reverse phase HPLC fingerprints of petroleum-base and of synthetic hydrocarbon-base fluids. The petroleum-base oil elutes as a broad band of unresolved peaks over the region between 500 and 850 seconds. The oxidation inhibitor BPC elutes with the base oil as a sharp peak at 650 ± 4 seconds, and the rust inhibitor elutes as a series of sharp and poorly resolved peaks in the early part of the chromatogram before 500 seconds. Since the antiwear agent TCP and the VI improver do not absorb strongly at the monitoring wavelength, they are not readily detectable nor apparent in the 6083D-0 fingerprint.

Upon examining the fingerprints, differences are evident that are directly related to chemical composition. For example, the fingerprints show that neither 5606C nor 83282A contain the barium dinonylnaphthalene sulfonate rust inhibitor. Also, the peak at about 647 seconds indicates that BPC is present in both 5606C and 6083C, but in appreciably smaller amounts than in 6083D-0. Comparing fingerprint 7c with 7d, it is obvious that exposing 6083D-0 to sunlight for one month

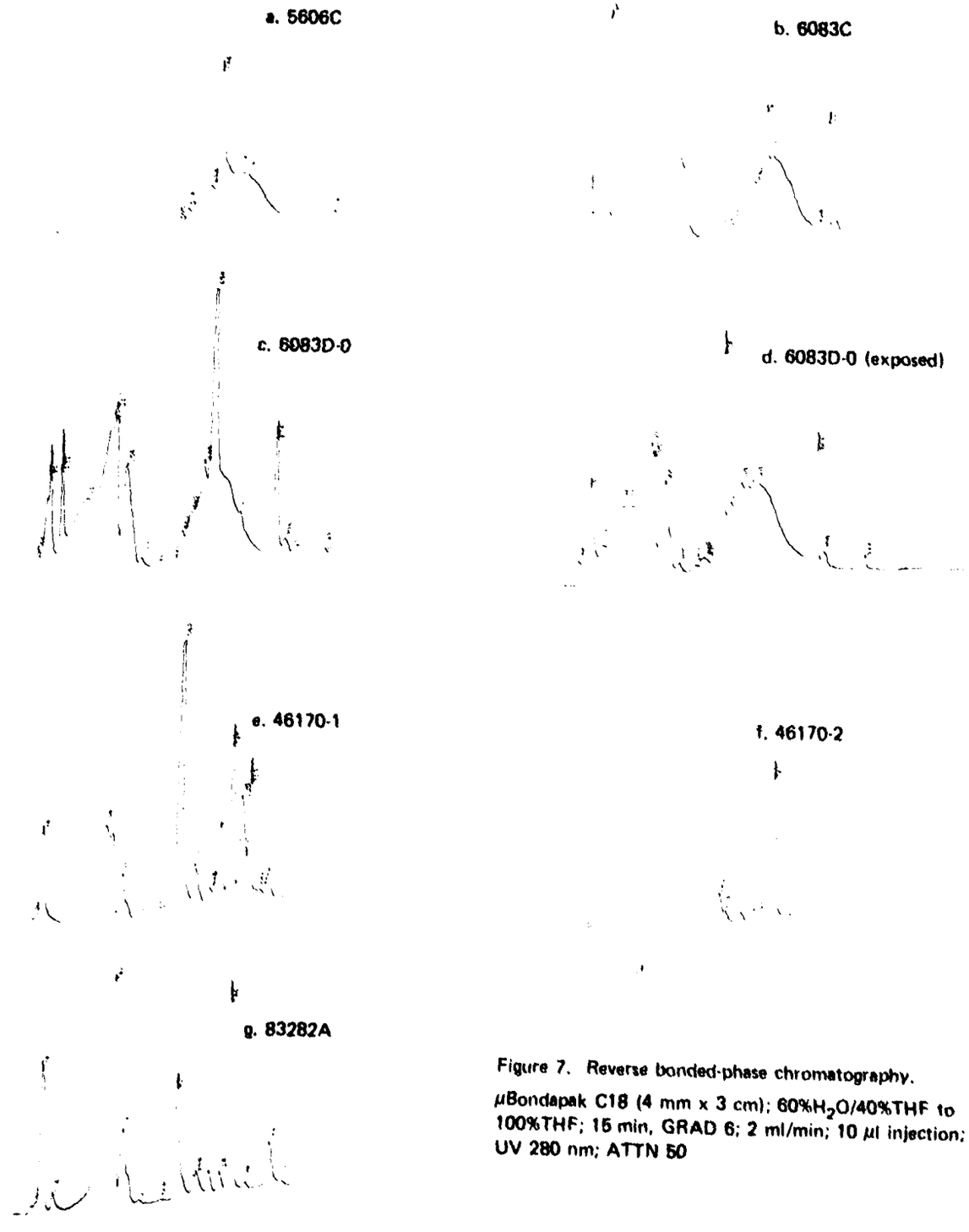

Figure 7. Reverse bonded-phase chromatography.

μBondapak C18 (4 mm x 3 cm); 60%H_2O/40%THF to 100%THF; 15 min, GRAD 6; 2 ml/min; 10 μl injection; UV 280 nm; ATTN 50

destroys or removes VPC and at least one other component (132 seconds). Other changes are apparent but most significant is the appearance of a new peak at 538 seconds which is probably a product of the oxidation inhibitor reaction.

Reverse bonded-phase chromatography with gradient elution is an excellent method for fingerprinting hydraulic fluid composition. A sufficient number of relatively sharp peaks are obtained to permit discrimination between different hydraulic fluids; e.g., 40170-1 and -2. In an attempt to develop methods for quantitatively analyzing specific fluid components, different mobile phases and solvent programs were evaluated. For petroleum-base fluids, base oil components were poorly resolved and generally interfered with the attempted analysis of other components. However, it was possible to obtain sharp, well-resolved peaks for synthetic hydrocarbon-type fluids indicating that such fluids are amenable to quantitative analysis.

IV. CONCLUSION AND SUGGESTED IMPLEMENTATION

HPLC is a viable analytical technique for monitoring the chemical compositions of hydraulic fluids. GPC provides a fingerprint dependent upon the relative size of hydraulic fluid component molecules in solution. The fingerprint obtained by normal phase adsorption chromatography depends mainly on polarity; whereas in reverse bonded-phase chromatography the separation and therefore the fingerprint is primarily based on the solubility of the hydraulic fluid components. Although all components generally cannot be monitored by a single fingerprint, hydraulic fluids are sufficiently complex that differences in composition can be discerned. Except for filtration no sample preparation is required. Less than 30 minutes are required to run an analysis on microliter size samples. The instrumentation is commercially available and requires little training for running routine analyses.

There are several limitations to the application of HPLC. Hydraulic fluid components must be soluble and not react with the solvent(s), column substrate, or instrument seals and tubing. Because of the nature of the column substrate materials employed, precautions must be taken to prevent irreversible adsorption of sample components and solvent contaminants. Uncontrolled adsorption may change column characteristics and result in incorrect analyses. Also, some components may prove too complex or be otherwise unsuitable (e.g., highly ionizable or associated species) to analyze by the methods developed herein. Although no problems were encountered with the fluids examined in this study, in most cases where problems arise it should be possible to modify the test methods to permit at least partial fingerprinting and quantitative analysis. Other limitations to the test methods developed for analyzing hydraulic fluids include the resolution and detection of specific components. Such problems are fundamental to the application of any liquid chromatographic method and are often reconcilable by the modification of test conditions.

Specific test methods were developed to fingerprint and quantitatively analyze the components in a MIL-H-6083D hydraulic fluid formulation. GPC, adsorption chromatography, and reverse bonded-phase chromatography methods were developed. Except for the VI improver analysis, GPC is not as definitive in fingerprinting or as useful in quantitative analysis as the other HPLC modes. Reverse bonded-phase chromatography with gradient elution is excellent for fingerprinting but is limited in

its usefulness for quantitative analysis of petroleum-base fluids because of the poor resolution and interference of the base oil. Adsorption chromatography is the most versatile HPLC mode for hydraulic fluid analysis. Definitive fingerprints are obtainable and it is possible to quantitatively analyze all the known components in sample 6083D-0 using a single set of columns with modifications in the mobile phase.

Total component analyses for a manufacturer's formulation and three in-house formulations of 6083D are shown in Table 8. The test method is indicated for each each analysis along with the standard deviation and an estimate of accuracy. Accuracy is defined as the average difference between the formulated and measured values. Except perhaps for the analysis of the base oil component, the repeatability and accuracy of the analyses are quite good. Indeed, the highest precision and accuracy are obtained in the analyses of the antiwear and oxidation inhibitor additives which each represent less than 1 wt % of the hydraulic fluid composition. It is noted that, although different test methods were employed to quantitatively analyze various components, the experimental values total to ca. 100 wt % as required for each formulation. Hence, within experimental error all components are accounted for.

It is concluded that the test methods developed for 6083D provide sufficiently distinct fingerprints and accurate component analyses to be used for fluid inspection and chemical specification. With the application of the methods, it would be practical to require more strict chemical specifications as part of MIL-H-6083D. Since MIL-H-6083D already requires the fluid manufacturer to supply samples of the base oil and additives used in formulating the fluid, it would be simple to implement the test methods. The supplied components could be used as standards for quantitative analysis and to define peaks in fingerprinting. Or primary standards may be used, if the chemical composition is specified to assure the quality of the supplied components.

The test methods are not limited to a single fluid type. Their application extends to all hydraulic fluids. For example, some specifications require that the fluid shall contain no VI improvers. Fluids could be tested for VI improvers using the procedures described in Appendix B. The TCP content is specified as 0.5 ± 0.1 wt % for several fluid types and could be accurately analyzed by the

Table 8. HPLC ANALYSIS OF 6083D FORMULATIONS

Component	Test Method (Appendix #)	WT% 6083D-0	6083D-1	6083D-2	6083D-3	precision	accuracy
V. I. improver	B2	13.3	14.0	14.0	11.1	0.2	0.3
base oil	D	78.5	79.6	79.6	84.5	2.4	1.4
TCP	G	0.470	0.501	0.504	0.401	0.004	0.01
BPC	F	0.90	0.92	0.88	0.74	0.02	0.1
rust inhibitor	E	5.2	6.1	6.1	3.7	0.1	0.5
total		98.4	101.1	101.1	100.4		

appropriate procedure (Appendix G). Also, fingerprinting by reverse bonded-phase chromatography (Appendix H) could be used to discern between fluids consisting of petroleum and synthetic base oils. In fact, any of the fingerprinting procedures (Appendixes A, C, and H) could be applied as a general test method to assure consistency of the fluid in successive batches.

The implementation of the HPLC test methods in Military Specifications for hydraulic fluids is suggested. In procurement, and HPLC fingerprint could be required of the supplier to assure a fluid's compositional integrity. HPLC inspection procedures may be used to verify that the correct hydraulic fluid is supplied and to determine whether different allotments of a fluid have compositional variations. HPLC could also be used to monitor hydraulic fluids stored for extended periods of time or exposed to unusual environmental conditions (e.g., high temperature and humidity or extreme cold). The fluids may be monitored for specific contaminants or chemical changes that are detrimental to the performance and maintenance of hydraulic systems. For example, a method has been developed for monitoring the oxidation inhibitor BPC. Since the depletion of BPC severely limits fluid lifetime, the HPLC method (Appendix F) could also be applied to ascertain the amount of oxidation inhibitor required to replenish the fluid.

The HPLC methods may be applied in a variety of field situations. Fluids in hydraulic systems may be sampled and inspected using HPLC to determine whether they require replacing. If a container of fluid is unlabeled or the type of fluid in a system is unknown, the fluid may be identified by HPLC fingerprinting. In changing over hydraulic systems from one type of fluid to another, complete fluid replacement may be assured by HPLC monitoring. HPLC may also aid in troubleshooting hydraulic system failures. Changes in fluid composition or detection of other substances (e.g., products of seal deterioration) may determine the cause and thereby help prevent future system failures.

Another area suggested for the implementation of HPLC is hydraulic fluid R&D to develop and improve new or modified fluids. Fluid stability and changes in fluid composition during accelerated testing could be monitored. Fluid compatibility, oxidative stability, etc., could be investigated. Because HPLC separation and detection is nondestructive, it is possible to apply preparative techniques and collect fluid components for purposes of identification. That is, unknown components or products resulting from chemical changes in hydraulic fluids may be separated by HPLC and identified using other techniques. For example, VI improvers may be quantitatively analyzed and isolated from other fluid components (Appendix B) and further characterized with respect to molecular weight and molecular weight distribution by GPC.[4] Hence, HPLC/GPC provides a means of assessing VI improvers by sampling fluids in operating hydraulic systems and evaluating the concentration and molecular weight distribution of the polymeric components(s).

ACKNOWLEDGMENT

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4. HOUSE, J. L, and HAGNAUER, G. L. *Compositional Analysis of Hydraulic Fluids Using Liquid Chromatography.* Army Materials and Mechanics Research Center, AMMRC TR 76-40, December 1976.

APPENDIXES

A. GPC FINGERPRINTING

This method provides a fingerprint of hydraulic fluid composition by gel permeation chromatography - GPC. In this technique, the hydraulic fluid or a solution of the hydraulic fluid is injected onto a chromatographic column (or series of columns) packed with porous substrate which separates sample component molecules according to their size in solution. The size-separated molecules are detected and recorded according to their retention time and concentration. Different detectors may be used to provide more definitive fingerprints.

The essential components of instrumentation are a solvent reservoir, a high performance solvent pumping system, a sample injection system, packed columns, chromatographic tubing with fittings, a solute detector and a plotter or strip chart recorder. Pre-packed columns and instrumentation are commercially available from a number of different manufacturers. However, variations exist in columns, instrumentation and designations for instrument settings (e.g., detector sensitivity settings). To avoid confusion, operating conditions and settings are designated with respect to the Waters ALC/GPC-244 instrument and the Spectra Physics SP4000 data system as described in Section II-C. Likewise, Waters Associates columns are designated since they were used to develop the test method. A 0-10 volt input card on the Spectra Physics SP4020 data interface is used to interface the SP4050 printer/plotter to the Waters model 440 UV absorbance detector output (0-2 volts). The Waters R400 RI detector output (0-100 millivolts) is interfaced using a 0-1 volt input card on the SP4020 data interface. For RI detection, both the RI detector sensitivity (e.g., 32X) and the SP4050 printer/plotter attenuation (e.g., ATTN 10) are specified in the test method.

The solvent and mobile phase is tetrahydrofuran (THF). Freshly distilled THF is recommended; however, THF with an antioxidant (0.025 to 0.1% hexene or t-butyl hydroxytoluene) to inhibit the formation of peroxides also may be used. The sample should be soluble in THF at room temperature. Both the solvent for the mobile phase and the sample or sample solution must be filtered through membrane filters with pore sizes of 0.5 μM. If the sample is fully soluble at room temperature, no solution preparation is required. However, if there is a question concerning solubility or if a larger injection volume is desired, a solution may be prepared by weighing the sample into a clean, dry volumetric flask and adding THF taken from the solvent reservoir to the calibrated volume mark.

Each high performance column is required to have a plate count equal to or greater than 3000 plates. A pure, low molecular weight compound is injected as a standard to determine the plate count. The following test conditions are recommended:

Mobile phase - THF
Flow rate - 2 ml/min
Temperature - ambient*

*The terms ambient and room temperature are defined as any temperature between 20 C and 30 C that is constant within ±1 C.

Standard - benzene
Injection volume - 1 µl
Detector - RI or UV
Recorder chart speed - 8 cm/min.

Plate count is calculated according to the equation

$$\text{plate count } N = 16\ (t_R/\Delta t)^2 \qquad \text{(A-1)}$$

where t_R is the retention time at the peak maximum of the standard and Δt is the peak width interval determined by calculating the time elapsed between the base-line intercepts of lines drawn tangent to the inflection points of the standard peak. Time units of either seconds or minutes may be used.

The test conditions for GPC fingerprinting of a THF soluble hydraulic fluid are:

Mobile phase - THF
Flow rate - 2 ml/min
Temperature - ambient
Columns - µStyragel 10^3, 500, 500, 100, 100 Å
Pump pressure - 1500 to 2500 psi
Injection volume - 5 µl
Detector - UV 280 nm, ATTN 10
- UV 254 nm, ATTN 10
- RI 32X, ATTN 10
Chart speed - 0.5 cm/min
Analysis time - 25 minutes.

GPC fingerprints are highly reproducible. A single run is sufficient to establish a fingerprint. Since the primary purpose of a fingerprint is to establish whether the chemical composition of a fluid has changed or is different from that of another fluid, a simple overlaying of chromatograms is generally sufficient. Fingerprint characteristics to be noted include (i) the number of peaks, (ii) peak retention times, (iii) peak heights or integrated peak areas, (iv) the ratio of a peak's height or area as determined with different detectors, (v) differences in peak shape, and (vi) the ratio of the height or area of one peak to other peaks in the same chromatogram. The extent of differences in hydraulic fluid composition can sometimes be judged by comparing peak areas or heights.

Refinements to the GPC method include using internal standards, automatic injection, data analysis and reporting systems and running additional analyses with different mobile phases and detectors (e.g., infrared detection with chloroform as the mobile phase).

As an alternative to high performance GPC, conventional Styragel columns may be used with a less sophisticated solvent pumping system.[4] The analysis time is longer, but the instrumentation is less costly than required for high performance GPC. The chromatograms are highly reproducible. Test conditions are:

Mobile phase - THF
Flow rate - 2.8 ml/min
Temperature - ambient
Columns - Styragel 100, 100, 100, 80-150 Å
(12 ft × 3/8 in.)
Pressure (columns and flow restrictor) - 450 psi
Injection volume - 0.2 ml
Detectors - RI, UV 254 and 280 nm
Chart speed - 0.4 cm/min
Analysis time - 45 min.

B. VI IMPROVER ANALYSIS

1. GPC Method

The concentration or relative concentration of VI improvers in hydraulic fluids is determined by this method. In this technique, the hydraulic fluid is injected onto a GPC column which size-separates the polymeric VI improver from other fluid components. The VI improver is detected using an RI monitor and is recorded or integrated according to its concentration. For quantitative analysis, a VI improver standard or hydraulic fluid standard of known formulation is required.

A variety of columns and instrumentation are commercially available which may be used for this analysis. A Laboratory Data Control model 709 solvent pumping station, flow restrictor, constant volume sample injector, and model 1103 RI detector were used to develop this method. The procedures described in Appendix A for solvent and sample handling also apply to this method. A static reference is used for RI detection and a Spectra Physics SP4000 data system is used for recording and integrating the VI improver peak. Test conditions are:

Mobile phase - THF
Flow rate - 3.3 ml/min
Temperature - ambient
Column - Styragel 80-150 Å (4 ft × 3/8 in.)
Injection volume - 0.2 ml
Detection - RI
Chart speed - 0.25 ml/min
VI improver retention time - 7.15 min
Analysis time - 14 min.

Since the VI improver elutes at the exclusion limit, its peak retention time is highly reproducible. Peak area integration is recommended for accurate analysis. The weight percent VI improver may be determined either from its integrated peak area or from the ratio of its area to the total area of all the peaks. A standard formulation of the fluid to be analyzed may be used for calibration. The procedure is:

Run the calibration standard three times and record the VI improver peak area A_S and the total peak area T_S.

Flush the sample injector with about 10 ml THF.

Run the unknown fluid three times and record the respective areas A_u and T_u.

Compute the average and standard deviation for each area.

If the repeatability is poorer than ±5%, run additional analyses or check the column and instrument operation.

Calculate weight percent VI improver as shown below

$$wt\ \% = \frac{A_u \cdot W_s}{A_s} \qquad \text{(B-1)}$$

and

$$wt\ \% = \frac{A_u \cdot T_s \cdot W_s}{A_s \cdot T_u} \qquad \text{(B-2)}$$

where W_s is the weight percent VI improver in the standard.

If the standard and unknown have chemically the same VI improver, Equation B-1 should provide an accurate analysis. If the values calculated from Equation B-1 and B-2 differ by more than 1 wt %, the VI improvers in the standard and the unknown may differ chemically and/or the composition and possibly the chemistry of other components in the fluids may differ significantly. This method is accurate to within 1 wt %.

If a sample of the VI improver is available, standard solutions (10-20 wt % VI improver in THF) may be prepared and run to obtain a calibration plot of weight percent versus peak area. If neither a VI improver nor a hydraulic fluid standard is available, the relative difference in VI improver concentration between samples may be determined. If an integrator is not available, peak heights rather than peak areas may be used in Equation B-1 with some loss in accuracy.

As a refinement to this method, the VI improver may be collected as it elutes from the detector and then injected onto GPC columns for high polymer characterization.[4] In this way, the average molecular weights and molecular weight distribution of the VI improver may be determined.

2. Adsorption Chromatographic Method

The concentration or relative concentration of VI improvers in hydraulic fluids is determined by this method. In this technique, the hydraulic fluid is injected onto a chromatographic column packed with polar, microporous silica substrate. THF is the mobile phase and RI detection is used to monitor the VI improver concentration. For quantitative analysis, a VI improver standard or hydraulic fluid standard of known formulation is required.

The instrumentation required is the same as described in Appendix A. The procedures for solvent and sample handling are also the same. Test conditions are:

Mobile phase - THF
Flow rate - 2 ml/min
Temperature - ambient
Column - μPorasil (30 cm × 3.9 mm)
Pump pressure - 1100 psi
Injection volume - 5 μl
Detector - RI 8X, ATTN 50
Chart speed - 1 cm/min
VI improver retention time - 58 seconds
Analysis time - 2 min.

The peak retention times are highly reproducible. Generally, only two peaks are observed - the VI improver peak eluting in what appears to be the interstitial volume of column packing and a peak composed of the nonpolymeric components. The procedures and calculations are essentially identical to the GPC method except that it is not necessary to flush the U6K sample injector with THF between analyses. Either peak areas or heights may be used in the calculations. For fluids with VI improver between 10 and 20 wt %, the precision is ±0.2 and ±0.4 wt % as determined by peak areas and heights, respectively. The analyses should be accurate to within 0.6 and 0.8 wt % for the peak area and height methods, respectively. The interpretation of data and refinements to the method are same as for the GPC method. As an additional refinement to improve precision, sample injection may be automated.

C. ADSORPTION CHROMATOGRAPHY FINGERPRINTING

1. Isocratic

This method provides a fingerprint of hydraulic fluid composition by adsorption chromatography. In this technique, the hydraulic fluid is injected onto a chromatographic column packed with a polar, microporous silica substrate. Separation depends upon specific interactions between solute components and the stationary phase with mobile phase molecules competing with the solute for adsorption sites. Separated molecules are detected and recorded according to their retention times and concentration. Different detectors may be used to provide more definitive fingerprints.

The instrumentation required is the same as described in Appendix A. The procedures for solvent and sample handling are the same except that "distilled-in-glass" methylene chloride is the solvent. A high performance column is required with a plate count equal to or greater than 3000 plates when determined according to the procedure recommended by the column manufacturer (Waters Associates, Manual No. CU 27386, September 1976):

Mobile phase - hexane
Flow rate - 7.5 ml/min
Temperature - ambient

Column - μPorasil (30 cm × 3.9 mm)
Standard - nitrobenzene
Injection volume - 1 μl or less
Detector - RI or UV
Chart speed - 8 cm/min.

Plate count is calculated according to Equation A-1.

The test conditions for fingerprinting the composition of a methylene chloride soluble hydraulic fluid are:

Mobile phase - methylene chloride
Flow rate - 2 ml/min
Temperature - ambient
Column - μPorasil (30 cm × 3.9 mm)
Pump pressure - 1100 psi
Injection volume - 5 μl
Detectors - UV 254 nm, ATTN 10 and/or UV 280 nm, ATTN 10
Chart speed - 1 cm/min
Analysis time - 5 min.

The fingerprints are generally quite reproducible. However, irreversible adsorption of very polar components can occur and may cause peaks to gradually shift to lower retention times. If such shifts are noted in repetitive injections of the same sample, this technique should not be used. As with the GPC fingerprinting method, an overlaying of chromatograms is generally sufficient to distinguish differences in composition between samples. Because sharp, well-resolved peaks are produced, an integrator or data system is especially useful for peak area analysis. Other refinements, such as mentioned in Appendix A, also may be applied to this method.

2. Gradient Elution

This method is similar to the isocratic method in Appendix C-1 except solvent programming is used to improve the resolution and promote complete elution of the sample components. In addition to the instrumentation described in Appendix A, a solvent programmer and an additional high pressure solvent delivery system are required. The solvents and samples are handled the same except that freshly distilled THF and "distilled-in-glass" 2,2,4-trimethylpentane (C8) are required for the mobile phase. A series of 3 μPorasil columns are used. The plate count per column and the procedure for determining the plate count is the same as that in Appendix C-1. The solvent is programmed from 100%C8 to 80%C8/20%THF using a linear solvent gradient (GRAD 6) initiated with sample injection and run for 5 minutes. The mobile phase is then held constant for at least 10 minutes to allow complete elution of the sample. The test conditions are:

Mobile phase - 100%C8 to 80%C8/20%THF, 5-min GRAD 6
Flow rate - 2 ml/min
Temperature - ambient
Column - μPorasil (90 cm × 3.9 mm)
Pump pressure - 1500 to 1400 psi
Injection volume - 5 μl

Detector - UV 280 nm, ATTN 10 and/or UV 254 nm, ATTN 10
Chart speed - 1 cm/min
Analysis time - 15 min.

After an analysis is completed, the mobile phase is returned to 100%C8 and at least 15 minutes are allowed for the columns to achieve equilibrium.

The fingerprints are highly repeatable when run on the same day with the same column set and with no changes in solvent supply. On successive days, peaks at higher retention times may shift by as much as 10 or 15 seconds. However, the general profile and characteristics of a fingerprint are maintained and irreversible adsorption is less likely to occur than when the isocratic method is used. Fingerprints are compared by overlaying chromatograms and noting fingerprint characteristics as discussed in Appendix A. Peak integration and other refinements, as mentioned in Appendix A, are applicable to this method.

D. BASE OIL ANALYSIS

The amount of petroleum-base oil in hydraulic fluids is estimated by this method. In this technique, the hydraulic fluid is injected onto a set of chromatographic columns packed with a polar, microporous silica substrate. Separation depends upon specific interactions between solute components and the stationary phase with mobile phase molecules competing with the solute for adsorption sites. A solvent gradient is programmed to facilitate separation and to sharpen component peaks. Separated molecules are detected and recorded according to their retention times and concentration. A standard of the same base oil stock that is used to formulate the hydraulic fluid is required for calibration.

The required instrumentation and the test conditions are identical to those described in the fingerprinting method (Appendix C-2). A UV 280-nm detector is used and a data system is required for peak integration. Calibration is achieved by spiking an aliquot of the hydraulic fluid with the base oil stock used in its formulation. The calibration sample is prepared by weighing w_x = 2g of the base oil stock with w = 10g of the hydraulic fluid and mixing in a 25-ml beaker. The procedure for base oil analysis is:

Run the base oil, the hydraulic fluid, and the hydraulic fluid calibration sample.

Consider the base oil portion of the chromatograms and select a well-resolved base oil component peak that can be monitored without interference by other components in the hydraulic fluid. If such a peak cannot be found, this method is invalid.

Set data system parameters for integration of the base oil peak.

Run the calibration standard three times and record the area A_s for the selected base oil peak.

Run the hydraulic fluid three times and record the area A for the selected base oil peak.

Compute the peak area average and standard deviation for each sample.

If the repeatability is poorer than ±5%, run additional analyses or check instrument operation.

With the assumption that base oil concentration is proportional to the area of the selected base oil component peak, the weight percent base oil is calculated as shown below

$$\text{wt } \% = \frac{w_x \cdot A}{w \cdot (A_s - A)} \cdot 100\%. \qquad \text{(D-1)}$$

The accuracy of this method depends upon the resolution of base oil component peaks and the overall composition of the hydraulic fluid to be analyzed. Because of the complexity of petroleum-base oils, this method is considered accurate only to within ±3 wt %. As a refinement, the test conditions may be modified as follows:

Mobile phase - 100%C8, after 10 min initiate a 5-min GRAD 6, programming the mobile phase from 100%C8 to 50%C8/50%THF
Detector - RI

All other conditions are identical to the original method.

By delaying the gradient and using RI detection in the initial part of the analysis, other, more prominent base oil components may be detected and UV absorbing, non-base oil components are less likely to interfere. After the base oil is monitored, the gradient rapidly eliminates other components in preparation for the next analysis.

E. RUST INHIBITOR ANALYSIS

The concentration of barium dinonylnaphthalene sulfonate rust inhibitor in hydraulic fluids is determined by this method. This method is identical to the method for base oil analysis except that the rust inhibitor standard is required for calibration. The rust inhibitor consists of a 50 wt % solution of barium dinonylnaphthalene sulfonate in solvent extracted castor oil. The calibration sample is prepared by weighing w_x = 0.5g of the rust inhibitor solution with w = 10g of the hydraulic fluid and mixing in a 25-ml beaker. The procedure is similar to the one used for the base oil analysis except that the rust inhibitor appears as a sharp, well-resolved peak at 308 ± 1 second. The repeatability of the integrated peak area is ±1.4% and the method is accurate to within ±0.55 wt %.

F. OXIDATION INHIBITOR ANALYSIS

The concentration of the oxidation inhibitor di-tert-butyl-p-cresol (BPC) in hydraulic fluids is determined by this method. This method is identical to the method for base oil analysis except that a BPC standard is required for calibration. Since part of the base oil elutes with BPC, the preferred method of calibration is to spike an aliquot of the hydraulic fluid with BPC. The calibration

sample is prepared by weighing w_x = 0.1g of BPC with w = 10g of the hydraulic fluid and mixing in a 25-ml beaker. The procedure is similar to the one used for the base oil analysis except that BPC appears as a sharp peak at 496 ± 2 seconds. The repeatability of the integrated peak area is ±2% and the method is accurate to within ±0.14 wt %. Depending on the condition of the columns and the purity of the solvents, the retention time of BPC may shift considerably. However, BPC has a large molar absorptivity at 280 nm and should be readily discerned when chromatograms of the spiked and unspiked samples are compared.

G. ANTIWEAR ADDITIVE ANALYSIS

The concentration of the antiwear additive tricresyl phosphate (TCP) in hydraulic fluids is determined by this method. This method is similar to the fingerprinting method described in Appendix C-1 except that a TCP standard is required for calibration.

The required instrumentation and test conditions are identical to those described in Appendix C-1. A UV 254-nm detector is used and the signal is recorded with an attenuation setting of 10. TCP elutes as a single, well-resolved peak at 275 seconds. Depending on the condition of the column, shifts in the retention time of TCP may be observed.

There are several alternatives to calibration and data analysis. Peak heights or integrated peak areas may be analyzed. If sample spiking is used for calibration, the calibration sample is prepared by weighing w_x = 0.1g of TCP with w = 20g of the hydraulic fluid and mixing in a 50-ml beaker. The procedure for TCP analysis is:

Run the calibration sample three times and record the TCP peak area A_s or peak height H_s.

Run the hydraulic fluid sample three times and record the TCP peak area A or peak height H.

If the repeatability is poorer than ±5%, run additional samples or check instrument operation.

Calculate weight percent TCP as shown below

$$\text{wt \% TCP} = \frac{w_x \cdot A}{w \cdot (A_s - A)} \cdot 100\% \qquad \text{(G-1)}$$

or

$$\text{wt \% TCP} = \frac{w_x \cdot H}{w \cdot (H_s - H)} \cdot 100\%. \qquad \text{(G-2)}$$

Alternatively, a calibration curve of peak area or height versus µg TCP may be constructed. Standard TCP solutions are prepared by adding weighed amounts of TCP to 100-ml volumetric flasks and diluting to the 100-ml mark with methylene chloride. Suggested concentrations for the standard solutions are 0.5, 1.0, 1.5,

and 2.0 mg/ml. After mixing, each standard solution is run with an injection volume of 25 µl. Peak areas or peak heights are recorded and plotted as a function of TCP injected. The hydraulic fluid may be analyzed directly or in methylene chloride solution. If direct analysis is desired, the hydraulic fluid is run three times with an injection volume V = 5 µl. The repeatability of peak areas or heights should be better than ±5%. Using the calibration plot, the average area or peak height is related to the weight w of TCP in the injected fluid sample and weight percent TCP is calculated using the relation

$$\text{wt \% TCP} = 100\% \cdot \frac{w}{V \cdot d} \qquad \text{(F-3)}$$

where d is the density of the hydraulic fluid in µg/µl units. Otherwise, a solution of concentration C (µg/µl) may be prepared by weighing 20g of the fluid sample into a 100-ml volumetric flask and diluting to 100-ml with methylene chloride. After mixing, V = 25 µl of the sample solution is injected and the weight percent TCP is calculated using the equation

$$\text{wt \% TCP} = 100\% \cdot \frac{w}{C \cdot V} \qquad \text{(F-4)}$$

where w is defined as above and is obtained using the calibration plot from the average peak area or height measurements of three runs.

For both the sample spiking and the solution standards methods of calibration, the precision is ±0.015 wt % and ±0.022 wt % TCP as determined by peak area and height measurements, respectively. TCP analyses should be accurate to within ±0.04 wt %.

The solution method may be modified to obtain higher precision by using benzyl alcohol as an internal standard. Benzyl alcohol is available in high purity and elutes as a fully resolved peak at 550 ± 5 seconds. A stock solution of the internal standard is prepared by pipetting 1 ml of benzyl alcohol into a 250-ml volumetric flask and diluting with methylene chloride to the 250-ml mark. The standard TCP solutions and hydraulic fluid sample solutions are prepared as described previously. A solution is prepared further for analysis by pipetting 10 ml of the standard or sample solution with 10 ml of the benzyl alcohol stock solution and mixing. The TCP- and fluid sample-internal standard solutions are run using an injection volume of 25 µl. Peak areas are recorded for the TCP and internal standard peaks and weight percent TCP is calculated using the equation

$$\text{wt \% TCP} = 100\% \cdot \frac{w \cdot \bar{A}_{IS,TCP}}{C \cdot V \cdot A_{IS}} \qquad \text{(F-5)}$$

where w, C, and V are as defined previously; $\bar{A}_{IS,TCP}$ is the average area of the internal standard peak as determined from the TCP standard solution analyses; and A_{IS} is the internal standard peak area obtained with the analysis of the fluid sample solution.

Using the internal standard method, TCP is determined with a precision of ±0.0051 wt % and an accuracy of ±0.012 wt %.

H. REVERSE BONDED-PHASE CHROMATOGRAPHY FINGERPRINTING

This method provides a fingerprint of hydraulic fluid composition by reverse bonded-phase chromatography. In this technique, the hydraulic fluid is injected onto a chromatographic column packed with a substrate of octadecylsilane C18 groups bonded on microporous silica. Separation depends upon the distribution of the solute between the mobile and bonded phases such that solutes more soluble in the bonded phase tend to have longer retention times. Solvent programming is used to enhance resolution and promote the complete elution of sample components. Separated molecules are monitored using a UV detector and are recorded according to their retention times and concentration.

In addition to the instrumentation described in Appendix A, a solvent programmer and an additional high pressure solvent delivery system are required. A solvent delivery system is dedicated to each solvent in the mobile phase which consists of THF and water. Both the THF and water must be freshly distilled and filtered under vacuum through 0.5 µM membrane filters. No solution preparation is required for samples soluble in THF at room temperature. Before injection, hydraulic fluid samples are filtered through 0.5 µM membrane filters. A high performance column is required with a plate count equal to or greater than 3000 plates when determined according to the following procedure:

Mobile phase - 40%H_2O/60% acetonitrile
Flow rate - 2.5 ml/min
Temperature - ambient
Column - µBondapak C18 (30 cm × 3.9 mm)
Standard - benzene
Injection volume - 1 µl or less
Detector - UV
Chart speed - 8 cm/min.

Plate count is calculated using Equation A-1.

The test conditions for fingerprinting the composition of a THF soluble hydraulic fluid are:

Mobile phase - 60%H_2O/40%THF to 100%THF, 15-min GRAD 6
Flow rate - 2 ml/min
Temperature - ambient
Column - µBondapak C18 (30 cm × 3.9 mm)
Pump pressure - 2500 to 700 psi
Injection volume - 10 µl
Detector - UV 280 nm, ATTN 50
Chart speed - 1 cm/min
Analysis time - 20 min.

The solvent is programmed from 60%H_2O/40%THF to 100%THF using a linear solvent gradient (GRAD 6) initiated with sample injection and run for 15 minutes. After an analysis is completed, the mobile phase is returned to 60%H_2O/40%THF and at least 10 minutes are allowed for the column to achieve equilibrium.

The fingerprints are highly repeatable and definitive. Fingerprints are compared by overlaying chromatograms and noting fingerprint characteristics as discussed in Appendix A. Peak integration and other refinements, as mentioned in Appendix A, are applicable to the method. The method may be modified by altering the solvent gradient, replacing THF with other organic solvents (e.g., acetonitrile) or using a different UV wavelength to monitor the column effluent. The usual precautions must be taken to assure the solubility and complete elution of samples.

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